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16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study.

The carbon black industry is a distinctive part of the chemical industry, which processes hydrocarbon feedstocks (mainly heavy oils) into finely divided carbon black particle for use largely in tires and, to a lesser extent, pigments, cement, and cosmetics. The industry sole products are various grades of carbon black. Two industrial process flow diagrams and four process descriptions have been prepared to characterize the industry. Within each process description available data have been presented on input materials, operating parameters, utility requirements and waste streams. Data related to the subject matter, including feedstock characteristics, company listings and atmospheric emissions are included as appendices.

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INDUSTRIAL PROCESS PROFILES
FOR ENVIRONMENTAL USE
CHAPTER 4
CARBON BLACK INDUSTRY

by

Richard W. Gerstle and John R. Richards
PEDCo-Environmental Specialists, Inc.
Cincinnati, Ohio 45246

Terry B. Parsons and Charles E. Hudak
Radian Corporation
Austin, Texas 78766

Contract No. 68-02-1319

Project Officer

Alfred B. Craig
Metals and Inorganic Chemicals Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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CARBON BLACK INDUSTRY

INDUSTRY DESCRIPTION

The carbon black industry is a distinctive portion of the chemical industry, which processes hydrocarbon feedstocks (mainly heavy oils) into finely divided carbon black particles for use largely in tires, and to a lesser extent, pigments, cement and cosmetics. The industry's sole products are various grades of carbon black. It is classified by the Department of Commerce under Standard Industrial Classification Code (SIC) 2895. Many of the companies involved in producing carbon black also produce other products, but these other products are independent of the carbon black process and are not related to this industry.

There are three ways of making carbon black, namely:

Furnace process

Thermal process

Channel process

The furnace process currently accounts for about 90 percent of production, with the thermal process accounting for most of the remaining 10 percent.^{1,2} The dominance of the furnace process is primarily due to the inherent flexibility to economically produce a wide variety of carbon black products.^{2,3} Products of the furnace and thermal processes have important physical differences (primary particle size) which affect the markets available. Generally these products do not compete for the same specific applications, therefore, the thermal and furnace plants are complimentary not alternative processes.

There is presently only one channel black plant in operation and it is subject to a court order requiring gradual closure during the next five years. This plant accounts for only 0.1 percent of domestic carbon black production.¹ Channel process plants have been replaced

with furnace process plants which can produce most of the same products without the major environmental problems associated with the older channel process.

Carbon black is currently manufactured at 33 locations in the United States. (One additional plant is currently not in operation.) These plants are mainly located in rural areas with only a few plants located near large population centers. Plants range in capacity from approximately 22.7 to 173×10^6 kg/year (25,000 to 190,000 tons). Capacity is, however, difficult to quantify since it is highly dependent on product characteristics, feedstock quality, and various operational factors. Total annual sales amounted to 1.4×10^9 kg (1,550,000 tons) in 1974,¹ which is approximately 70 percent of industry capacity.¹ This is somewhat below the average capacity factor of 80 percent.⁴ Near term industry growth will be accomplished primarily through plant modifications.⁴ No new carbon black plants are anticipated in the next several years.⁴

The domestic carbon black industry is not threatened by foreign imports. Furthermore, there is no generally acceptable substitute for carbon black in major applications such as automobile tires and colorants. For these reasons, steady growth of the domestic industry is expected. The growth rate predictions, however, are uncertain since this industry is closely tied to the automobile industry. A significant change in automobile sales or a increased demand for small cars would have a potentially large influence on carbon black demand.⁴ Approximately 94 percent of domestic production in 1974 were used in the automobile industry. A 3 percent carbon black industry rate is predicted for the next four years.¹

Total employment in the carbon black industry is too small to be tabulated on a routine basis,⁵ but it is probably on the order of 1000 to 1500 plant personnel.

Raw Materials

Furnace process plants utilize oil as the main feedstock for production of carbon black and use varying quantities of natural gas for heat and process control.⁴ The most desirable feedstocks are high aromatic oils with low sulfur content. In the thermal process, natural gas is the only raw material.

Liquid feedstocks are transported by rail, barge, and tank truck. The environmental impact connected with feedstock production occurs at the petroleum refinery. Transportation of the feedstocks does not entail any impact other than those associated with internal engine fuel combustion. Oil spills from oil transfer operations and storage facilities can occur accidentally. There are no fugitive emissions.

Natural gas is conveyed by pipeline, and does not cause any unusual environmental impact during its transportation. Example feedstock compositions are provided in Appendix A.

Products

Carbon black products have a high degree of diversity with respect to physical properties and applications. The main property affecting the characteristics is the particle size of the carbon particles. Mean particle size varies from 100 to 4000 Å^a in diameter.² Due to the effect on rubber characteristics³; carbon black particle products are sometimes described as "soft" or "hard". The degree of particle agglomeration ("structure") is a second physical characteristic of importance. All carbon black products are essentially pure carbon with trace amounts of sulfur and some organic compounds.

The physical properties now serve as the basis for an ASTM product classification system developed in 1968. This is a four digit alpha-numeric code representing particle size and curing rate.⁶ This system replaces a more cumbersome code which was more closely related to the influence of the carbon black on rubber characteristics.

^aOne angstrom is equivalent to 1×10^8 centimeters.

Companies

Eight companies produce carbon black in the United States as shown in Table 1. This table also shows the percent of total industry capacity by company. A number of these companies are closely associated with petroleum companies since the required feedstock is derived from petroleum refining.

A complete list of plants, their locations and capacities is included in Appendix B.

Table 1. CARBON BLACK PRODUCERS

Company	% of furnace black capacity	% of thermal black capacity
Ashland Chemical Company Division of Ashland Oil Co., Inc.	16.0	-
Cabot Corporation	23.9	28.7 ^a
Cities Service Company, Inc. Columbian Division	21.2	15.8
Commercial Solvents Corporation Thermatomic Carbon Co. Division	-	43.0
Continental Carbon Company	11.3	-
J. M. Huber Corporation	10.0	12.5
Phillips Petroleum Company	12.4	-
Sid Richardson Carbon Company	5.2	-

^apresently shutdown.

Environmental Impact

o Furnace Process - Gaseous emissions of carbon monoxide and hydrogen sulfide constitute the primary environmental problems associated with furnace process plants. Other atmospheric emissions include small quantities of particulate and hydrocarbons (primarily acetylene).

The concentrations and quantities of CO emitted are intimately related to the type of carbon black product. Generally the quantity of CO evolved during the cracking process is inversely proportional to the particle size of the final product. Emissions range between 0.8 to 3.0 kg per kg of black for typical products.⁴ Despite the much higher CO emissions from fine particle black process lines, the stack concentration is generally lower than larger particle black lines due to the greater burden of water vapor and other inert gases. The off-gas concentration can vary from 3 to 7 percent, 78,000 to 18,200 mg/m³ (30,000-70,000 ppm), with the lower values corresponding to fine particle black process lines. This dilution factor, necessary for the production of small particle blacks, reduces the heat content of the off-gas thereby complicating pollution control. Meteorological dispersion modeling of a hypothetical carbon black plant (125,000 ton per year capacity) suggest that National Air Quality Standards for CO will probably be violated in the vicinity of the plants.⁴ Due to the high CO levels in the plant off-gas; stack sampling personnel should have special training before attempting any tests.

The hydrogen sulfide emissions are closely related to the sulfur content of the feedstock. The prevailing trend is toward higher sulfur content feedstocks due primarily to the shortage of more desirable oil supplies. It is anticipated that the sulfur content will gradually increase from the present 1 to 2 percent by weight levels to a 2 to 3 percent by weight range in the near future.⁴ This could substantially increase present H₂S emissions, estimated at 0.03 kg per kg of black and 130 to 2600 mg/m³ (50 to 1000 ppm)(v/v).⁴ Other sulfur compounds emitted may include carbon disulfide (CS₂) and carbonyl sulfide.⁴ Hydrogen sulfide odors are apparent in the vicinity of some carbon black plants.

Particulate emissions are generally highly controlled due to both economic considerations and environmental control requirements. Effluent from the fabric filters contain particulate concentrations in the range of 0.068 to 0.295 g/DNm³ (0.03 to 0.13 grains/dscf) and represent approximately 0.001 to 0.005 kg per kg of black.⁴ Despite these low emission rates, some concern has been expressed due to the

potentially carcinogenic character of emissions from cracking processes. A number of toxicological and analytical studies⁷⁻¹⁶ have been done, however, no clear results are apparent. The analytical studies have demonstrated the presence of between 7 and 20 known carcinogens however, there is a serious question whether these compounds can be released to body fluids. Due to the large surface area of carbon blacks it is conceivable that the carcinogenic action is precluded by strong adsorption of the compounds on the surface of the carbon black particles. Investigations have generally been unsuccessful both in identifying the PAH compounds in fluids exposed to carbon black and in inducing cancer development in animals. Additional study is necessary to clarify the potential carcinogenic characteristics of various grades of carbon black. The industry deserves considerable credit for sponsoring early work in this subject area well before there was national interest in environmental control.

Hydrocarbons comprised mainly of methane and acetylene ore emitted at a rate of 0.03 to 0.26 kg per kg of black. Off-gas concentrations are 0.15 to 0.85 percent, 3900 to 27,100 mg/m³ (1500-8500 ppm). These two hydrocarbons should not contribute significantly to photochemical oxidants in the general vicinity of the plant since both are much less reactive than most hydrocarbons. The impact of such emissions, however, during long range transport is less certain since even very slow photochemical reactions could be of significance.

Only a few furnace process plants presently utilize off-gas combustion in order to reduce emission of CO, H₂S and other pollutants. Previously, control applications have been limited to installations where there is a local market for the excess steam energy which can be generated in a CO boiler. There is now a trend toward use of more off-gas as a supplemental fuel in pellet driers and toward the use of CO boilers on new process lines equipped with the necessary mechanical steam driers for use of the generated steam. This trend is due to both environmental considerations and the rising cost of all forms of energy. In most properly designed combustion devices (including pellet driers and CO boilers) the control efficiencies for CO, H₂S

and hydrocarbon approach 99 percent. Thermal incineration^a yields the same control efficiencies without benefit of energy recovery. In all three types of control devices, small quantities of SO₂ and NO_x are generated. SO₂ emissions can be increased from essentially zero to 0.02 kg per kg of black and to a concentration of 780 mg/m³ (300 ppm). Nitrogen oxide emissions are estimated to increase from approximately 26 mg/m³ (10 ppm), in the reactor, to 182 mg/m³ (70 ppm) leaving the control device (0.0002 to 0.003 kg per kg of black).

The furnace process operates without any major liquid process waste since it is basically a gas phase process. Wet scrubbers occasionally used to control atmospheric particulate emissions recover a useful product, therefore, such effluent is generally utilized either in the quench system or the pelletizer so that the black will reenter the process stream. Boiler blowdown is the only liquid waste commonly discarded.

There are no major solid waste associated with the furnace process. Limited amounts of refractor material, scrap, and worn fabric filter bags must be discarded in landfill. The quantities are insignificant. There is growing interest over the long term in the use of waste tires as a substitute feedstock at carbon black plants. This could partially alleviate one of the major solid waste problems in the United States.

o Thermal Process - Thermal process plants utilize a cleaner feedstock and can recycle all of the off-gas to reactors to recover the heating value (due primarily to H₂). Environmental control is an inherent part of the process, therefore, emissions are generally considered insignificant. Aqueous and solid waste quantities are also very small.

^aFlares are also utilized, however, control efficiencies and exit pollutant concentrations are not well known due to the difficulty in sampling.

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INDUSTRY ANALYSIS

The analysis of the carbon black industry is logically divided into discussions of the furnace and thermal processes. Recognizing that the furnace process accounts for 90 percent of domestic carbon black production and a much greater share of the environmental impact, aspects relative to the furnace process are emphasized.

Process flow sheets have been prepared for each of the major processes. These are highly generalized and have been arranged to highlight environmental impact. In certain cases a series of major steps have been combined into blocks in order to yield one distinct pollutant source. Despite the apparent simplicity of these flowsheets, it should be appreciated that the industry is extremely diverse with respect to equipment design, process operation and product characteristics. Due to these differences it is extremely difficult to characterize the capacity of a single process line of a plant overall. Furthermore, each process has the capability to produce a variety of carbon black products. Therefore, the information provided with respect to utilities, impact materials, and operating conditions is not necessarily applicable to any one process line or plant.

Most of the information contained in the following section has been obtained by PEDCo-Environmental Specialists, Inc. and Air Products, Inc. (Houdry Division) during recent EPA Contract studies. The PEDCo study served as the basis for an EPA Standard Support Document for the Furnace Black industry. This report is the primary reference for this industry analysis.

Trends in the carbon black industry will have a major influence on the environmental impact and energy impact of this industry. The carbon black industry is unique with respect to the close relationship between

pollutant emissions and energy use since the primary pollutants have a substantial heating value. The relationship, however, is highly complex and deserves considerably more discussion than is possible in a catalog summary. Under certain circumstances, the combustion of off-gas pollutants can simultaneously reduce pollutant emissions and reduce the demand for electrical energy in the plant. Conversely, some plants with a low Btu content off-gas cannot burn the off-gas without a substantial increase in supplemental fuel (mainly natural gas or distillate oil). While secondary combustion always reduces environmental impact, the resulting energy impact can range from moderately positive to substantially unfavorable. Due to the dual importance of environmental and energy problems, this aspect of carbon black production is given emphasis.

Furnace Process

The generalized flowsheet for the furnace process is shown in Figure 1. Carbon black is produced by the cracking of oil feedstock in a series of reactors. Some natural gas is used to heat the vaporized oil to the necessary reactor temperature. Product characteristics are controlled by a variety of proprietary operating procedures which generally involve means to change residence time in the cracking zone of the reactor. Primary quench can be done to abruptly terminate quenching. Subsequent quench cooling to less than 500 F is necessary to protect downstream fabric filters for product recovery. Both quench processes are included in the first block along with the fabric filter. This block essentially comprises 80 percent of most existing plants since only pelletizing and product storage are not included.

It should be noted that the fabric filter is generally considered an integral part of the carbon black plant since it serves as the only means of product recovery from the reactor gas stream. Present fabric filter, however, are probably over-designed from a purely economic standpoint, since somewhat greater product losses could be tolerated. Environmental regulations are responsible for the very high efficiency necessary.

Product yield is generally defined as the quantities of carbon black produced per unit quantity of carbon in the feedstock. A different basis has been used for expressing emission quantities and other factors in the subsequent process description. These factors are described (unless otherwise stated) in terms of quantity per unit quantity of product. The revised basis is considered more useful to persons interested in environmental control who do not have routine access to data concerning feedstock characteristics.

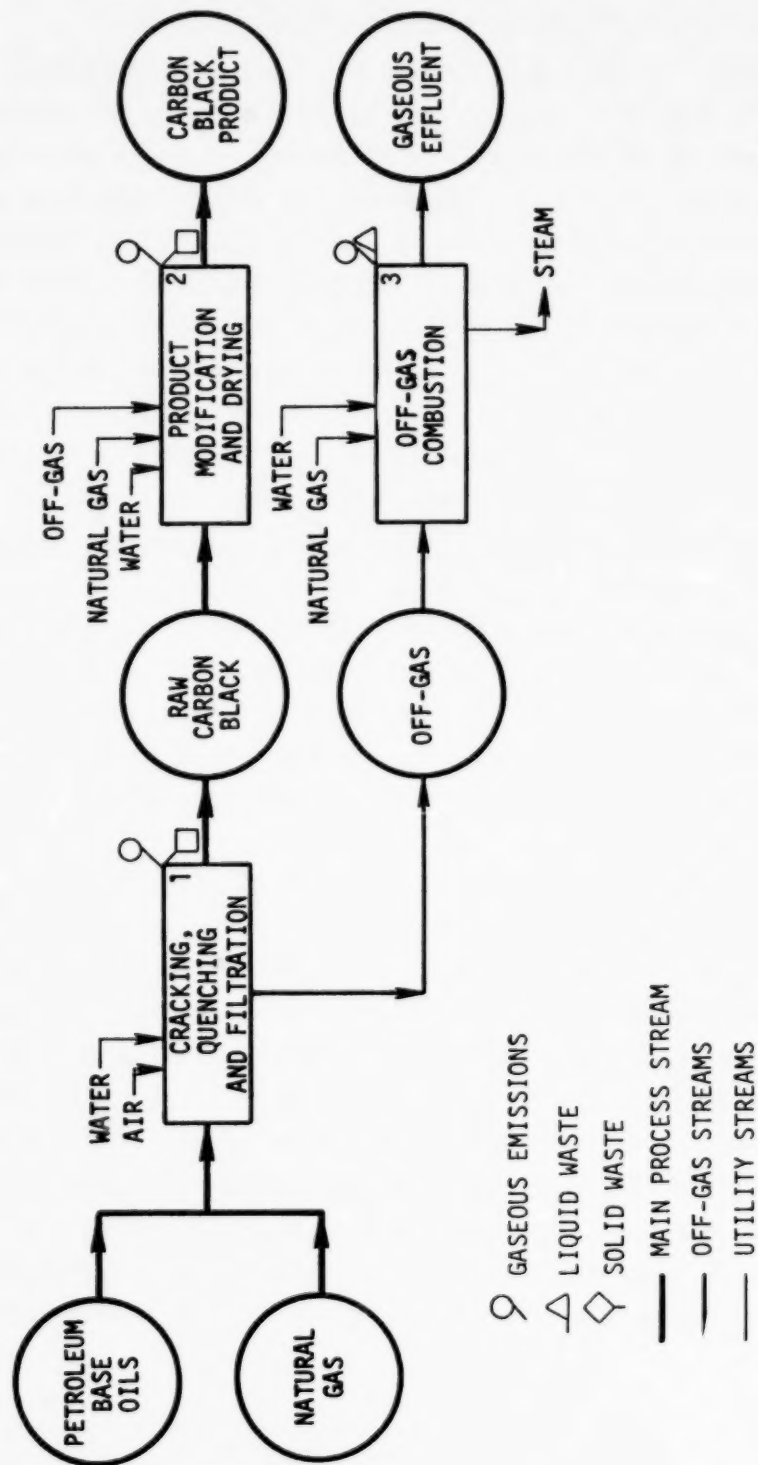


Figure 1. Furnace process flowsheet.

Cracking, Quenching and Filtration

1. Function - This process involves the incomplete combustion and thermal cracking of a liquid hydrocarbon feedstock at a temperature of approximately 1400°C to produce an aerosol of carbon particles. The gaseous effluent from the reactor undergoes primary quenching with water to reduce gas temperatures to approximately 540 C, thereby stopping the cracking reactions. Secondary quenching is done to further reduce temperature to less than 500 F in order to protect the fabric filter. Condensation of corrosive gases occurs if the temperature drops below 400-450 F.¹ The particulate (raw carbon black) is then removed from the gas stream by passage through a multi-compartment fabric filter system. A number of reactors (2 to 10) are normally manifolded together and served by a single quench chamber and product collection system.^{1,2,3}

2. Input Materials - The main input materials include an oil feedstock with natural gas for heat and product quality control.^{2,3} Highly aromatic oil is desired due to high product yields, and the low endothermic heat requirements.¹ Refinery by-product residuum tars are commonly used as feeds. Sulfur contents in the range of 1 to 3 percent are encountered.¹

The consumption of feedstocks per unit of product varies with the desired product characteristics. Reported yields are in the range of 0.5 to 0.65 kilogram of product per kilogram of carbon in feed for the larger sized blacks, and 0.2 to 0.3 for very small particle blacks.^{1,3}

3. Operating Parameters - Operating conditions will vary from plant to plant and within a given plant depending on the grade of product manufactured. Details of reactor operation and exact feed rates are proprietary, but generally speaking, the smaller the carbon black particle size being made, the higher the necessary air-to-oil ratio, and the lower the yield of black (kg of product per kg of carbon in feedstocks). While it is not possible to define "representative" reactor operating

conditions, example reactor feed rates and temperatures are presented in Table 2 for illustrative purposes.

Table 2. EXAMPLE OPERATING CONDITIONS FOR A REACTOR²

Parameter	Value
Rate of feed oil	757 liter/hour (200 gallons/hour)
Preheat temperature of oil	260 C
Rate of air supplied	1.8 m ³ /sec (235,000 cfh)
Rate of natural gas supplied	0.17 m ³ /sec (22,000 cfm)
Furnace temperature in reaction zone	1400 C
Rate of carbon black production	390 kg/hour (860 lbs/hour)
Yield of black (kg of product in 100 kg of C in feedstock)	60%

After the gases leave the reactor they are cooled, and enter a multicompartment fabric filter containing tube type fiberglass bags. Silicon-graphitized and Teflon[®] coatings have been used to improve filter performance. Bag life varies from 9 to 30 months.¹ Filtering velocities are low relative to some of the fabric filter applications with air-to-cloth ratios varying from 1.0 to 1.7 cubic meters per minute per square meter of fabric area.¹ Maximum pressure drop is in the range of 150 to 250 millimeters of water (6 to 10 inches). Cleaning of compartments is normally done on a 2 to 10-minute cycle by reversing the gas flow.¹

4. Utilities - Natural gas is considered as a feed stream and not a utility. The following approximate utility rates are required:

Electricity	0.22 kWh/kg (200 kWh/ton of product)
Water	6 l/kg (1450 gallons/ton of product)

[®]Registered trademark.

5. Waste Streams - The major waste stream from this process is the atmospheric emission of CO, gaseous hydrocarbons, particulates, and H₂S. These emission levels are:

<u>Pollutant</u>	Pollutant quantity ¹ in off-gas (kg/kg of product)	Pollutant concentration ¹ in off-gas μg/m ³
CO	0.8-3.0	3.4×10^7 to 8.0×10^7
Hydrocarbons	0.07-0.1	1.5×10^6 to 8.5×10^6
Hydrogen Sulfide	0.005-0.013	7.0×10^4 to 1.0×10^6
Particulate	0.001-0.003	not applicable
Sulfur Dioxide	trace	trace to 3.93×10^5
Nitrogen Oxide	≈0.0002	9.8×10^5 to 1.2×10^5

The carbon monoxide emissions vary according to the type of carbon black product being produced. Very small particle blacks generally result in high emission quantities and somewhat lower pollutant concentrations. Similar trends occur for hydrocarbons and to a limited extent hydrogen sulfide. The apparent inconsistency is due to the greater gas volumes in the fine particle black process lines.

The hydrogen sulfide emissions are closely related to the feed-stock sulfur content.

The particulate emission depend primarily on the particle characteristics and the condition of the fabric filter. Particle size distribution data is not presently available. Gaseous hydrocarbons consist almost entirely of methane and acetylene. Limited quantities of polynuclear organic matter (POM) may also be emitted.¹

There is no liquid waste from this process except for yard storm water runoff and boiler blowdown.

Solid waste is generated to a very limited extent by the disposal of used fabric filters and refractory bricks. This is usually disposed of in a landfill. This material amounts to about 0.5 to 1.0 gm/kg of product (1.0 to 2.0 pounds per ton) with about 30 percent due

to the fabric filter.¹

6. EPA Source Classification Code (SCC)

Furnace process - Oil feed	3-01-005-04
Furnace process - Gas and oil feed	3-01-005-05
Furnace process - Gas feed	3-01-005-03

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Product Modification and Drying

1. Function - Raw carbon black leaving the filtration step, is pulverized to break up any agglomerates; pelletized to facilitate handling, and finally dried prior to storage and shipment. Pulverizing is accomplished in a micropulverizer. The carbon black in the fluffy state is then wetted and pelletized with water in a pin or finger-type agitator. Pellets in the 40 to 60 mesh size, containing 30 to 40 percent water, are formed. The pellets then enter a combined direct, indirect-fired, rotary drum type dryer. Natural gas is used as a fuel and in some plants this is supplemented with process off-gas. A portion (35 to 70 percent) of the hot dryer combustion gases are passed directly through the rotary drum to remove the evaporated water. These purge gases containing particulate matter are vented through fabric filters similar to those used in Process No. 1 but generally smaller.

2. Input Materials - Raw carbon black is the main feed material to this process. Varying quantities of water are used for wetting the carbon black and natural gas is used as a heat source.

3. Operating Parameters - Product preparation is conducted at atmospheric pressure. The pulverized black at a density of 80 to 192 kg/m³ (3 to 12 pounds/ft³) is pelletized to a density of 320 to 560 kg/m³ (20 to 35 pounds/ft³).^{2,3} The drier is operated at a temperature of 175 to 260 C.¹ A maximum of 75 percent of the natural gas required for the drier can be replaced using off-gas from Process No. 1. Extensive modification to the drier combustion chamber must generally be done to accomodate the lower heat content off-gas fuel. Only 10 to 20 percent of the total off-gas can be consumed in pellet driers.

4. Utilities - The following approximate utility rates are required:

Electricity	0.0165 kWh/kg of product (15 kWh/ton of product)
Heat	390 kcal/kg of product (1.4 × 10 ⁶ Btu/ton of product)
Water	0.54 l/kg of product (130 gallons/ton of product)

5. Waste Streams - The purge gas from the drier contains particulate matter. These emissions are always controlled to recover the carbon black, and an average emission rate of 0.04 gm/kg (0.08 pounds per ton) of product results.¹ If a scrubber is used to control these emissions, the liquid effluent is used in the pelletizer and no liquid waste occurs.

Some solid waste in the form of "off-spec" product results from this process. This material is sent to a storage silo and usually blended back into the product at a low rate.

6. EPA Source Classification Code - None exists.

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3. Mantell, C. L. Carbon and Graphite Handbook. Wiley and Sons, Inc., 1968.

Off-Gas Combustion

1. Function - This process consists of a combustion device used to recover heat from the off-gases and/or to reduce emissions of CO, HC and H₂S. The off-gases from Process No. 1 are burned in either a CO boiler, incinerator, flare or some combination of these devices. When a boiler is used, steam is generated. However, a typical carbon black plant can utilize only 40 to 60 percent of the steam that is generated when all of the off-gases are burned.¹ For a typical size carbon black plant it is estimated that 2500 to 5300 horsepower hours per hour of electrical energy can be generated through combustion of off-gas. Steam can only be utilized for pump and fan drives, or to preheat feedstock.

2. Input Materials - Process off-gas and natural gas are the two main feed materials. The chemical characteristics of the off-gas determine how much, if any, supplemental fuel in the form of natural gas is required to ensure combustion. The Btu content of various grades of carbon black are presented below based on data in reference 1.

<u>ASTM product code</u>	<u>Typical particle size mu</u>	<u>% of total production</u>	<u>Btu/scf</u>
N-1xx	11-19	1.0	36
N-2xx	20-25	9.7	39
N-3xx	26-30	44.0	45
N-4xx	40-48	12.8	45
N-5xx	49-60	27.0	45
N-6xx	61-100	10.5	55

At a Btu/scf level of approximately 50 (actual levels depend on CO content, H₂ content and H₂O burden), an off-gas can be burned without any supplemental fuel. Natural gas requirements increase substantially as the heat content drops below 45 Btu/scf.

It should be noted that use of a high temperature fabric filter (not yet technically feasible) would conceivably eliminate the need for secondary quenching in Process No. 1. This would have a double

benefit since the off-gas temperature to the off-gas combustion system would be as much as 300 C hotter and would have a higher heat content due to less H₂O. Supplemental fuel requirements could probably be substantially reduced or eliminated at most present and future plants if such air pollution control technology was developed.

3. Operating Parameters - The type of control device will dictate the exact operating conditions. Generally a fire-box temperature of about 980 C (1800 F) is maintained to ensure good combustion.¹ Flares probably operate at a lower temperature, but quantitative data are not available.

4. Utilities - Auxiliary fuel in the form of natural gas is the primary utility required for off-gas combustion. This fuel requirement will vary with the CO content of the off-gas as described above. It should be noted that off-gas combustion has not been done as the very low Btu content off-gas used to represent an upper limit. The lower range of fuel requirements are representative of presently operating systems.

Electricity 0.002 to 0.004 kWh/kg of product
 (2 to 4 kWh/ton of product)

Fuel 800 to 15,800 kcal/kg of product
 (3 to 60 × 10⁶ Btu/ton of product)

Water 4.1 to 8.3 l/kg of product
 (1000 to 2000 gallons/ton of product)

5. Waste Streams - Trace amounts of CO, hydrocarbons and particulate are emitted to the atmosphere. In addition, any H₂S present is converted to SO₂ and some NO_x is formed. These emissions are summarized in the table below (source, Ref. 1).

<u>Pollutant</u>	<u>Pollutant quantity</u> <u>kg/kg of product</u>	<u>Pollutant concentration</u> <u>µg/m³</u>
CO	0.005	2.3 × 10 ⁵
Hydrocarbons	0.004	1.7 × 10 ⁴
Hydrogen sulfide	< 0.0003	< 1.4 × 10 ⁴
Particulate	0.0010	5.0 × 10 ⁴
SO ₂	0.0180	8.5 × 10 ⁵
NO _x	0.0030	8.6 × 10 ⁴

At these emission levels, meteorological models suggest that ambient air quality standards for CO will not be exceeded or approached. Furthermore, H₂S will be well below the odor threshold. The impact of the SO₂ emissions could conceivably contribute to a local SO₂ problem in certain cases.

There is no solid waste from this system. Liquid effluent occurs when a steam boiler is used since boiler blowdown is required. This amounts to approximately 5 percent of the steam generated.

6. EPA Source Classification Code - None exists.

7. References

1. An Investigation of the Best Systems of Emission Reduction for Furnace Process Carbon Black Plants in The Carbon Black Industry. Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, Environmental Protection Agency, April 1976.

Thermal Process

The generalized flowsheet for a thermal process carbon black plant is shown in Figure 2. Since there are no substantial environmental impact, the entire plant is shown as one process block. Unlike the furnace process plants, pelletizing is not normally done since thermal blacks are inherently larger in size and easier to handle. Also, an off-gas combustion process is not necessary since the reactor is utilized for energy recovery.

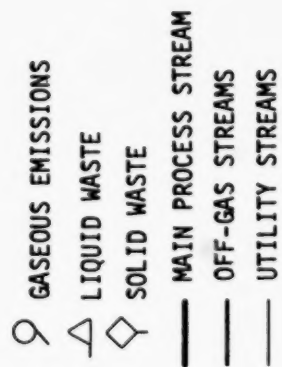
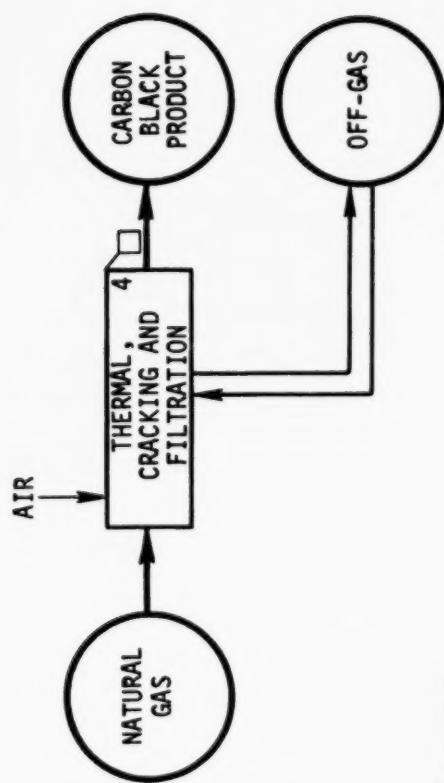


Figure 2. Thermal process flowsheet.

Cracking and Filtration

1. Function - In the thermal process, decomposition of a gaseous hydrocarbon feed is produced by thermal cracking in the absence of air to yield carbon and hydrogen. The product stream is then filtered to remove carbon black and the exit gas is burned to generate heat for additional cracking.
2. Input Materials - Natural gas is used as the input feedstock. Yields of 0.4 to 0.5 kg of product per kg of natural gas feedstock are achieved.¹ This is equivalent to 8.7 cubic meters of natural gas per kg of product (13 cubic feet per pound).¹ Hydrogen from the cracking reaction, washed and compressed, is used as a fuel to provide heat.
3. Operating Parameters - The cracking chamber operates at a temperature of 1315 to 1540 C (2400 to 2800 F).¹ Two refractory-lined cylindrical furnaces (generators) are employed for the reaction. The generators, about 12 feet in diameter and 25 feet high, are nearly filled with an open checkerwork of silica brick. This checkerwork is first heated by burning hydrogen generated in the decomposition reaction and/or by additional gas fuel. While one set of checkerwork is decomposing gas to produce carbon black, the other set is being heated by burning the off-gas. The gas flows are then switched and the heating/decomposition cycle is repeated every 10 minutes. The decomposed gas is then cooled by water sprays to 125 C, and the carbon black removed by a series of cyclones and fabric filters.
4. Utilities - Electricity and water are required in this process. Electrical requirements can be minimized by utilizing steam driven pumps and fans. This steam can be generated on-site since an excess of hydrogen is produced, and this can be utilized as fuel. If steam is not generated on-site, the utility requirements will be similar to those encountered in the furnace process, namely:

Electricity	0.22 kWh/kg of product (200 kWh/ton of product)
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Water 6 l/kg of product
 (1450 gallons/ton of product)

5. Waste Streams - Atmospheric emissions are very low since the off-gas is recycled and burned to provide heat for cracking, or sent to a boiler as fuel. Some particulate emissions occur when the reactors are switched from the cracking to the heating cycle. This puff of carbon black is caused by particulate buildup on the checkerwork.

There are no other waste streams except for solid waste in the form of old fabric filters and refractory bricks.

6. EPA Source Classification Code - Thermal black process (gas feed)
3-01-005-2.

7. References

1. Kirk-Othmer Encyclopedia of Chemical Technology, Volume 4.

APPENDIX A
FURNACE BLACK FEED CHARACTERISTICS

Table A-1. TYPICAL FEED OIL CHARACTERISTICS

Property	Typical Range
Specific gravity at 60 F	1.0 to 1.1
A.P.I. at 60 F	-2.9 to 10
Carbon, %	90 to 91
Hydrogen, %	7.3 to 8.2
Sulfur, %	1 to 2.5
Ash, %	0.002 to 0.02
Sodium, %	0.2 to 0.8

Note: Coal tar products are used by some European plants, but are not used in the United States. Due to a shortage of feedstocks, carbon black plants are being forced to utilize feedstocks with ever increasing sulfur content even though this is not desirable from a product quality standpoint. Sulfur content increases from 0.85 percent to 1.50 percent have occurred at some plants. Feedstocks with 2 to 3 percent sulfur are not uncommon. Limited supplies and increased cost of natural gas has also led to greater dependence on liquid feeds.

Table A-2. TYPICAL NATURAL GAS COMPOSITION

Component	Mol %
Nitrogen	2.41
Carbon dioxide	0.41
Methane	91.81
Ethane	4.83
Propane	0.49
Iso-Butane	0.02
M-Butane	0.03
Iso-Pentane	Trace
M-Pentane	Trace

APPENDIX B
COMPANY LISTING

Table B-1. CARBON BLACK PLANTS - 1974

Company	Plant Location	Annual ^a Capacity Millions of Pounds
A. FURNACE PROCESS		
Ashland Chemical Company Division of Ashland Oil Company, Inc.	Aransas Pass, Texas	154
	Belpre, Ohio	67
	Ivanhoe, Louisiana	240
	Mojave, California	68
	Shamrock, Texas	109
Cabot Corporation	Big Spring, Texas	200
	Franklin, Louisiana	384
	Pampa, Texas	60
	Villa Platte, Louisiana	196
	Waverly, West Virginia	112
Cities Service Company Columbian Division	Conroe, Texas	110
	El Dorado, Arkansas	98
	Eola, Louisiana	66
	Franklin, Louisiana	214
	Mojave, California	50
	Moundsville, West Virginia	150
	Seagraves, Texas	95
Continental Carbon Company	Ulysses, Kansas	60
	Bakersfield, California	71
	Phenix City, Alabama (shutdown)	50
	Ponca City, Oklahoma	122
	Sunray, Texas	97
J.M. Huber Corporation	Westlake, Louisiana	109
	Bayton, Texas	266
Phillips Petroleum Company	Borger, Texas	132
	Borger, Texas	318
	Orange, Texas	95
Sid Richardson Carbon Co.	Toledo, Ohio	80
	Addis, Louisiana	80
	Big Spring, Texas	120
TOTAL Furnace Black		3,981 (92%)

^aStated capacities are approximate since they depend on type of product.

Table B-1 (Continued). CARBON BLACK PLANTS - 1974

Company	Plant Location	Annual ^a Capacity Millions of Pounds
B. THERMAL PROCESS		
Cabot Corporation	Big Spring, Texas (shutdown)	100
Cities Service	Franklin, Louisiana	55
Commerical Solvents Corporation Theratomic Carbon	Sterlington, Louisiana	150
J.M. Huber Corporation	Borger, Texas	44
TOTAL Thermal Black		349 (8%)

^aStated capacities are approximate since they depend on type of product.

APPENDIX C
ATMOSPHERIC EMISSIONS

Table C-1. TYPICAL ATMOSPHERIC EMISSIONS FOR A 90 MILLION POUND PER YEAR CARBON BLACK PLANT^d

Component	Range, mol, %	kg/hr	Typical kg/kg of product	Mol, %
Hydrogen	2.7-7.5	559	0.11	6.7
Carbon dioxide	1.5-3.3	4,336	0.91	2.5
Carbon monoxide	3-7	6,396	1.3	5.5
Hydrogen sulfide	0.005-0.1	139	0.03	0.1
Sulfur oxide	TR-0.015 ^a	TR	-	TR
Methane	0.1-0.35	145	0.03	0.2
Acetylene	0.05-0.5	174	0.03	0.2
Nitrogen	32.5-40	41,221	8.2	35.5
Oxygen	0-2.5	368	0.07	0.3
Nitrogen oxide	8-100 ppm ^a	8	-	44 ppm
Particulate	0.048 gr/scf ^c	11	0.002	0.048 gr/scf ^c
Water	42-50	36,465	7.3	49
Total		89,822	18.0	100

^aMost data is near low side of range.

^bAfter fabric filter with 99.78% control. Reactor effluent contains 5,016 pounds of carbon black per hour.

^cIncluding water vapor.

^dAn Investigation of the Best Systems of Emission Reduction for Furnace Process Carbon Black Plants in the Carbon Black Industry. Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, Environmental Protection Agency, April 1976.